

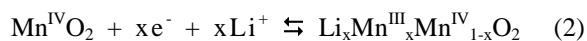
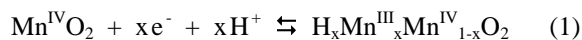
Spectroelectrochemical Characterization of Cation-Insertion Reactions at Nanostructured, Mesoporous Manganese Oxide

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Transition metal oxides that are mixed ion-electron conductors are of great technological interest for such electrochemical applications as batteries,¹ ultracapacitors,² and fuel cells.³ The utility of these materials is based on their ability to undergo cation/electron insertion reactions. Properties such as charge/discharge rate and reversibility are optimized when the metal oxide is prepared as a nanostructured material.

Sol-gel chemistry provides a flexible route to the synthesis of nanostructured oxides, offering the advantage of intimate mixing of reactants on the molecular level. Sol-gel methods are also easily adaptable for the preparation of thin films. The high surface areas and interconnected mesoporosity of the wet gels can be retained in the dry state if the pore fluid is removed under supercritical conditions (to form an aerogel), or as a low surface tension liquid under ambient-pressure conditions (to form an ambigel).⁴

Manganese oxide is an important cathode material both for the alkaline Zn/MnO₂ cell and for lithium and lithium-ion cells, where charge storage is accomplished by cation/electron insertion with either H⁺ or Li⁺.



Nanostructured manganese oxide can be derived from a variety of sol-gel formulations, and can be obtained in more than 25 different polymorphs. Mesoporous manganese oxide ambigels and aerogels have been previously described.^{5,6,7}

We report the preparation of manganese oxide ambigels and aerogels both as monoliths and as thin films supported on indium-doped tin-oxide (ITO) glass. Based on the reduction of permanganate by fumaric acid, we obtain manganese oxide gels in either the K⁺-compensated cryptomelane form or the Na⁺-compensated birnessite form. Physical characterization is obtained for material derived from gel monoliths using such techniques as N₂ physisorption, high-resolution transmission microscopy, and thermal analysis.

Manganese oxide is an anodically coloring electrochromic material, where the conversion of Mn (IV) to Mn (III) during the cation-insertion process is accompanied by a decrease in the optical absorbance. We exploit these electrochromic properties in the characterization of cation-insertion reactions at ITO-supported films of manganese oxide ambigels and aerogels. Whereas the electrochemical response (current, charge) at these high surface area materials is complicated by such effects as double-layer charging and electrolyte decomposition, the optical absorbance responds only to changes in the electronic state of the manganese oxide.

Using spectroelectrochemical techniques we explore the insertion properties of manganese oxide ambigels and aerogels with such technologically relevant cations as Li⁺, Mg²⁺, and Al³⁺. Spectroelectrochemistry

provides valuable information regarding such properties as cation-insertion rates and reversibility. We also utilize bulky, organic tetraalkylammonium cations to further discriminate among the various energetic sites (surface, vacancies, interlayer) available for cation association at these nanostructured manganese oxide domains.

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